was treated as described before for the magnesium system, determining the $[\alpha]/[\beta]$ ratios from double intergration and $[\alpha + \beta]$ from total spin concentration. When $\ln K'_{\mathrm{diss}}$ was plotted vs. $1/T$, a straight line was indeed obtained from the slope of which a ΔH_{diss} value of -3.9 ± 0.2 kcal/mol was determined. The fact that such a good linear correlation was observed is good evidence that the assumption of ionic association being weak is valid for $Ca(ClO_4)_2$–HMPA solutions.

N⁻·–Ba²⁺–HMPA. As with the other alkaline earth cation perchlorate salts, addition of $Ba(ClO_4)_2$ to a solution containing the ninhydrin anion radical results in the appearance of an additional superimposed and time-resolved ESR spectrum. This new spectrum predominates and is observed exclusively after addition of a stoichiometric excess of the salt. The new spectrum consists of a sharp pentet (peak-to-peak line width of <0.1 G) with a coupling constant of 0.93 G, due to the accidental degeneracy of all four hydrogens in the aromatic ring. The spectrum of the ion pair is displaced 1.03 G to higher magnetic field relative to the center of the spectrum for the free anion radical (see Table I). Temperature variation between 0 and 100 °C failed to reveal any line-width phenomenon, an indication that the ion pairs present in solution interconvert very rapidly on the ESR time scale.

Since $Ba(ClO_4)_2$ has been shown to exist fully dissociated in HMPA,[10] determination of ΔH_{diss} was straightforward as described for the previous cases. The value determined was -2.1 ± 0.6 kcal/mol, slightly more positive than that for the calcium ion pair.

From the results presented here it is clear that Mg^{2+}, due to its high charge/size ratio, forms the strongest ion pair with N⁻·, as judged by the ΔH_{diss} value. The other two cations exhibit very similar behavior, where ion-pair dissociation is slightly exothermic.

Registry No. Ba, 7440-39-3; Ca, 7440-70-2; Mg, 7439-95-4; ninhydrin anion radical, 75275-60-4.

Hydrogen Bonding in Low-Temperature Matrices: 1. Proton Donor Abilities of Fluoroalcohols. Comparative Infrared Studies of ROH···O(CH₃)₂ Complex Formation in the Gas Phase, in CCl₄ Solution, and in Solid Argon¹

Otto Schrems,* Helmut M. Oberhoffer,† and Werner A. P. Luck

Fachbereich Physikalische Chemie der Universität Marburg, D-3550 Marburg, Federal Republic of Germany
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The proton donor–acceptor complexes formed by a series of fluoroalcohols with systematically increasing acidity (pK_a's from 14.5 to 5.4) have been studied with dimethyl ether (DME) as a reference base in argon matrices, in CCl_4 solutions, and in the gas phase. The intermolecular bond formation O–H···O is discussed on the basis of changes of the O–H stretching absorptions in the infrared spectra. A stepwise increase of the proton donor abilities of the fluoroalcohols is achieved by successively introducing fluorine in β-position of the alcohols as indicated by the increasing frequency shift of the O–H stretching vibrations in the O–H···O complexes. The observed frequency shifts $\Delta\nu$ increase as one passes from the gas phase to CCl_4 solutions and argon matrices. Data for $\Delta H°$, $\Delta S°$, and $\Delta G°$ have been derived from the solution measurements on the basis of the temperature-dependent intensity changes of the "free" O–H stretching bands. A comparison of the O–H stretching frequencies of the alcohol monomers obtained from the three phases has also been made. The small shifts observed in argon matrices on the order of 19 ± 4 cm⁻¹ are characteristic for weak interactions of the van der Waals type. The solvent shift in CCl_4 is about twice as high and was found to be on the order of 45 ± 8 cm⁻¹, indicating a much stronger interaction with the solute molecules. It is concluded that it is advantageous, where possible, to study a particular hydrogen-bonded system in different phases in order to get a deeper insight into intermolecular interactions ranging from very weak to very strong and to distinguish hydrogen bond interaction in condensed phases from other intermolecular forces or environmental effects.

Introduction

The unique value of matrix isolation spectroscopy in studying hydrogen bond interactions has been demonstrated already in the classic papers by Van Thiel, Becker, and Pimentel on water[2] and methanol[3] and the applications of this novel technique have been growing ever since. The matrix isolation technique not only enables vibrational spectra to be obtained for monomeric, dimeric, trimeric, and higher associated hydrogen-bonded species and can thus elucidate the structure of clusters but also allows the study of unstable species as well as proton transfer reactions. Many of these aspects are particularly interesting since they bridge the gap in understanding differences between the structures of "unperturbed" dimers in the vapor phase and the structure of the pure liquid and solid.

In contrast to liquid solutions in which the IR absorption bands due to hydrogen-bonded multimeric species are usually very broad,

considerable narrowing occurs on condensation in low-temperature matrices. Spectral features due to self-association can be identified from their concentration dependence and from annealing experiments in which monomers diffuse and form small clusters. Small clusters of molecules can serve as useful models for understanding more complicated systems such as hydrogen-bonded liquids.[4] Theoretical treatments of hydrogen-bonded complexes examine the clusters free from any interaction with other molecules.

* Present address: Department of Chemistry, University of California, Berkeley, CA 94720.
† Present address: Institut für Physikalische Chemie der Universität Bonn, Wegelerstrasse 12, D-5300 Bonn, Federal Republic of Germany.

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Therefore, for direct comparison with theoretical predictions vibrational spectra of hydrogen-bonded complexes should ideally be obtained at low pressures and low temperatures in the gas phase. However, experimental difficulties like low vapor pressures of the substances, low concentrations of the complexes, overlapping rotational structure, etc. are limiting factors for gas-phase studies. However, many of these problems can be overcome nowadays by supersonic molecular beam techniques, where the internal degrees of freedom and the molecular vibrations and rotations have been cooled to very low temperatures.

Most of the hydrogen bond infrared studies have been performed in solutions of inert solvents. Spectra of complexes in solutions are usually much easier to obtain, but complicated by the interactions with the solvent. Moreover, the large bandwidths of the hydrogen-bonded modes make it virtually impossible to identify bands due to multimers of definite size. Band breadth is troublesome even in solutions of nonpolar solvents. For example, at high concentrations in carbon tetrachloride solutions, alcohols exhibit spectra with a very broad absorption band centered at about 3350 cm^{-1} in the O–H stretching region comparable to those of pure liquids. Although the advantages of the matrix isolation technique are unique and it overcomes many of the difficulties mentioned above, one has to keep in mind that matrix-isolated species are of course not completely free of interactions with the matrix environment. Thus, experimental studies of hydrogen-bonded complexes comparing results from the gas phase, liquid phase (solutions), and solid phase (low-temperature matrices) are extremely valuable, but still fairly rare.[5] This mainly is due to the fact that there are not too many systems which are amenable to study in all three phases. Such types of studies, however, are needed for the understanding and correct interpretation of results obtained from any of these phases.

An understanding of the infrared spectra in terms of the various environmental effects on the solutes is vital, since the spectra of many of the species studied by the matrix isolation technique are previously unknown or markedly different from those in other phases. Neglect of the possibilities of spectral changes caused by the environment, particularly of matrix effects, however, can lead to misinterpretations of the observed spectra. Therefore, there is an essential need for systematic and careful studies in order to get a better knowledge of how the changes of phase and the changes of the environment provided by the matrix materials can influence the monomeric and associated species.

Hydrogen bonding between alkanols and some fluoroalcohols as proton donors and ethers as proton acceptors has been studied in the gas phase[6-8] and in binary and ternary solutions.[9-19] In a previous paper[20] we discussed the complexes of methanol with dimethyl ether (DME) and of ethanol with diethyl ether in argon matrices.

In this paper we report our results from studies of ROH···O-

$(CH_3)_2$ complexes obtained from the gas phase, CCl_4 solution, and argon matrices. With alcohols of the type R_3COH ($R = H$, CH_3, CH_2F, CHF_2, CF_3) as proton donors one has an excellent series of model complexes, where the proton donor strength is systematically varied (up to nine fluorine atoms in β-position) without changing the donor group.

The purpose of the present work is manifold: (i) systematical study of the hydrogen bonding abilities of fluoroalcohols by changing the number of fluorine substituents; (ii) comparison of the spectral properties of the hydrogen-bonded complexes from the different phases such as the frequency shifts $\Delta\nu_{OH}$, band profiles, band intensities, and band multiplicities; (iii) correlation of the hydrogen bond energy (ΔH), Taft substituent parameter σ^*, and the acidity of the alcohols (characterized by their pK_a values) with the frequency shifts $\Delta\nu_{OH}$ of the ROH···O$(CH_3)_2$ complexes.

Experimental Section

The gas-phase measurements have been performed with a variable-temperature gas cell of our own design with an optical pathlength of 100 mm. The cell consists of a glass cylinder surrounded by a glass jacket for the thermostatting liquid. It is fitted with KBr windows, gas inlet and outlet tubes for evacuation and admission of samples, as well as a side arm for condensation of samples. A MKS Baratron pressure gauge (Type 220) from MKS Instruments was attached to the cell in order to measure the partial pressures of the components and the total pressure of the mixtures. Measurements of the pressures are believed to be accurate within ±0.1 torr, temperatures within ±0.2 °C. The partial pressures of the single components were kept low enough to avoid self-association of the alcohols and were 20 torr or lower.

The solution spectra were recorded with home-made stainless steel liquid cells (KBr windows) in the temperature range −20 to +20 °C. The cell in the reference beam contained dimethyl ether in CCl_4 at the same initial concentration as in the sample cell. Temperature cycling has been applied in recording the spectra. At the beginning and at the end of the experiments the spectra were scanned at 20 °C to reensure the reliability of the measurements. Since the measurements were carried out in very dilute solutions, the self-association of the fluoroalcohols was negligible. In all cases the alcohol concentration was 0.01 M and the concentration of dimethyl ether was 0.05 M. Therefore, in the mixtures the 1:1 complexes between the alcohols and the ether could be considered the only complexes of importance. Diluted dimethyl ether solutions were prepared by dissolving dimethyl ether (DME) from a gas cylinder in carbon tetrachloride cooled to −20 °C. The ether concentration was determined by checking the weight increase of the CCl_4 solution. All substances used were kept over molecular sieves (3 Å) before use to eliminate water traces.

The gaseous mixtures for the matrix studies were prepared by standard manometric procedures in a stainless steel vacuum system, which was previously pumped down to 10^{-7} torr by means of a Pfeiffer-Balzers turbo molecular pump (Type TPH 200 S). An excess of DME was used in the mixtures in order to minimize self-association of the alcohols in the matrices and to increase the probability for the formation of ROH···O$(CH_3)_2$ 1:1 complexes. The gas mixtures were continuously sprayed onto a CsI window maintained at 6 K through a capillary (diameter = 0.3 mm) at a deposition rate below 1 mmol h^{-1}. The experiments were performed with a liquid transfer Heli Tran system (Air Products Model LT-3-110 B). The temperature was measured with an Fe–Au (0.07% Fe) vs. chromel thermocouple. Annealing experiments were performed with a resistance heater, mounted at the cold tip.

All spectra have been recorded with a Perkin-Elmer 325 grating spectrometer. Spectral slit widths were about 1 cm^{-1} in the 4000–2000-cm^{-1} range and the frequency accuracies are about ±1 cm^{-1}. The alcohol samples (99.5%) and CCl_4 were Uvasol grade and obtained from E. Merck, Darmstadt and Aldrich, Milwaukee. 2,2-Difluoroethanol (DFE) has been synthesized from difluoroacidic acid with LiAlH$_4$ as reducing agent according to

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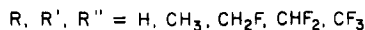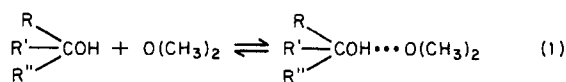(20) W. A. P. Luck and O. Schrems, *Spectrosc. Lett.*, **13**, 719 (1980).
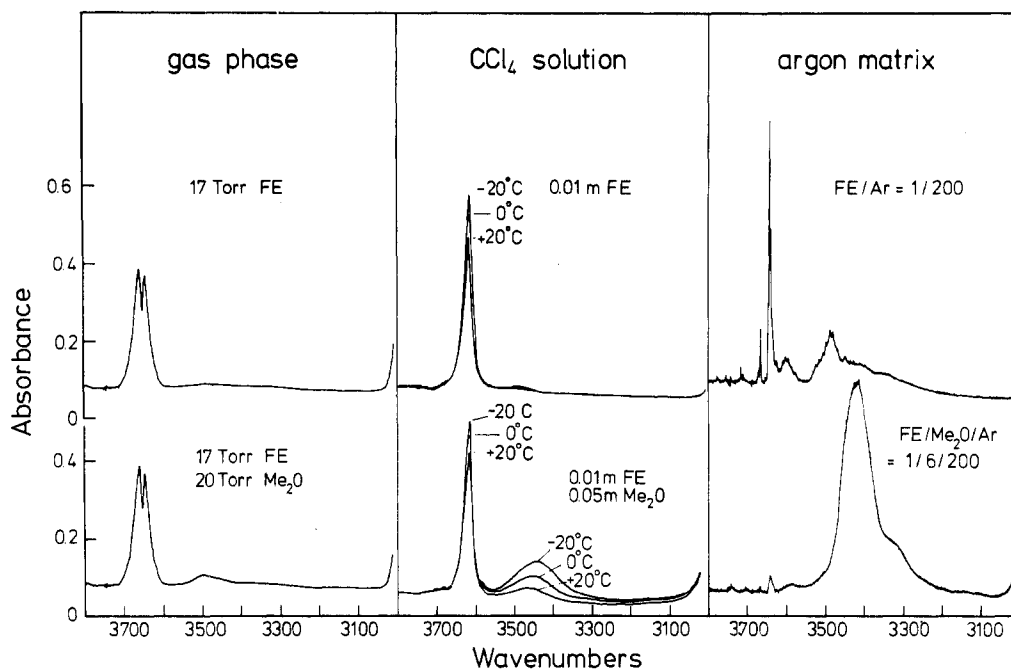
Figure 1. Infrared spectra of 2-fluoroethanol (FE) in the gas phase (17 torr of FE, $T = 35$ °C, $d = 100$ mm), in CCl_4 solution (0.01 M, $T = -20$, 0, +20 °C, $d = 5$ mm), and in an argon matrix (FE/Ar = 200, $T = 6$ K) in the O–H stretching region (upper part) and spectra of mixtures of FE (17 torr) with DME (20 torr) in the gas phase ($T = 35$ °C, $d = 100$ mm), FE (0.01 M) with DME (0.05 M) in CCl_4 ($T = -20$, 0, +20 °C, $d = 5$ mm), and FE with DME in an argon matrix (FE/DME/Ar = 1/6/200) at 6 K (lower part).

the method described by Middleton et al.[21] Dimethyl ether (99.8%) and argon (99.997%) were obtained from Messer Griesheim, Düsseldorf.

Results and Discussion

Hydrogen-bonded complexes with fluoroalcohols as proton donors and dimethyl ether (DME) as a standard reference base have been studied in the gas phase, in CCl_4 solutions, and in argon matrices (eq 1). The number of fluorine atoms attached to the

$$R' {\Large\rightleftharpoons} COH + O(CH_3)_2 \rightleftharpoons R' {\Large\rightleftharpoons} COH \cdots O(CH_3)_2 \quad (1)$$

$$R, R', R'' = H, CH_3, CH_2F, CHF_2, CF_3$$

alkyl group of the alcohols has been systematically increased in order to enhance the donating capacity of the proton donor molecules. By that means it became possible to vary the hydrogen bond strength in related complexes over a wide range without changing the atoms directly involved in the hydrogen bond (O–H⋯O). Since the O–H stretching vibrations are the most sensitive modes in hydrogen bond formation we have been mainly concerned with the displacement $\Delta\nu_{OH}$ of the complexes from that of the free alcohols and the band profiles of the absorptions.

Measurements in the Gas Phase

As a preliminary step for understanding the spectra of the complexes, the spectra of fluoroalcohols were examined at pressures of 20 torr, or lower. Vapor pressure limitations did not arise for most of the alcohols and varying the temperature only changed the intensities but not the band profiles. Self-association of the alcohols can therefore be excluded under the experimental conditions applied here (see Figures 1–3). Some vapor infrared spectra of the fluoroalcohols studied are described in the literature,[22-28] but some remarks should be made concerning the O–H

stretching band profiles of the free alcohols. 2-Fluoroethanol (FE) shows a doublet at 3660 and 3648 cm^{-1} which must be, in accordance with Buckley et al.,[24] ascribed to the O–H stretching mode of one isomer (the gauche obviously) since it shows no temperature effect whatsoever over a wide temperature range. The separation of the doublet is suitable for the P and R branches of the O–H stretching band in the free molecule. Similar arguments may hold for the doublet of 2,2-difluoroethanol (DFE) at 3662 and 3650 cm^{-1} for which no literature data were available. 2,2,2-Trifluoroethanol (TFE) exclusively exists in the gauche form in the vapor state. In the case of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) the doublet at 3665 and 3625 cm^{-1} (see Figure 3) is caused by conformational heterogeneity and intramolecular interactions as described by Barnes et al.[26] and Murto et al.[27] The higher frequency absorption is obviously due to a conformer with the OH group in a position to interact with one CF_3 group (C_1 conformer), the lower frequency component to a conformer with the OH group in a position to interact with both CF_3 groups (C_s conformer). For perfluoro-*tert*-butyl alcohol (PFTB) there is experimental evidence that only one conformer predominates in the vapor state as already reported by Murto et al.[28] with the O–H stretching frequency located at 3630 cm^{-1}. PFTB is a highly interesting compound as it is the most highly fluorinated alcohol and as its pK_a is about 5.4 at 25 °C; the alcohol is almost as strong an acid as acetic acid. DME, the proton acceptor used to form O–H⋯O complexes, does not have any absorptions which might interfere in the range of the OH bands of the complexes. Figures 1–3 show some typical spectra, namely, those for FE, TFE, and HFP as single components and as mixtures with DME. New O–H absorptions are observed in the presence of DME indicating the formation of ROH⋯O(CH$_3$)$_2$ complexes. It should be noted that some of the complex bands are nearly symmetric whereas others have an asymmetric band structure. Plausible reasons for these observations are conformational heterogeneity, combinations with external modes, or contributions due to higher associated complexes. However, under the experimental conditions used, the last

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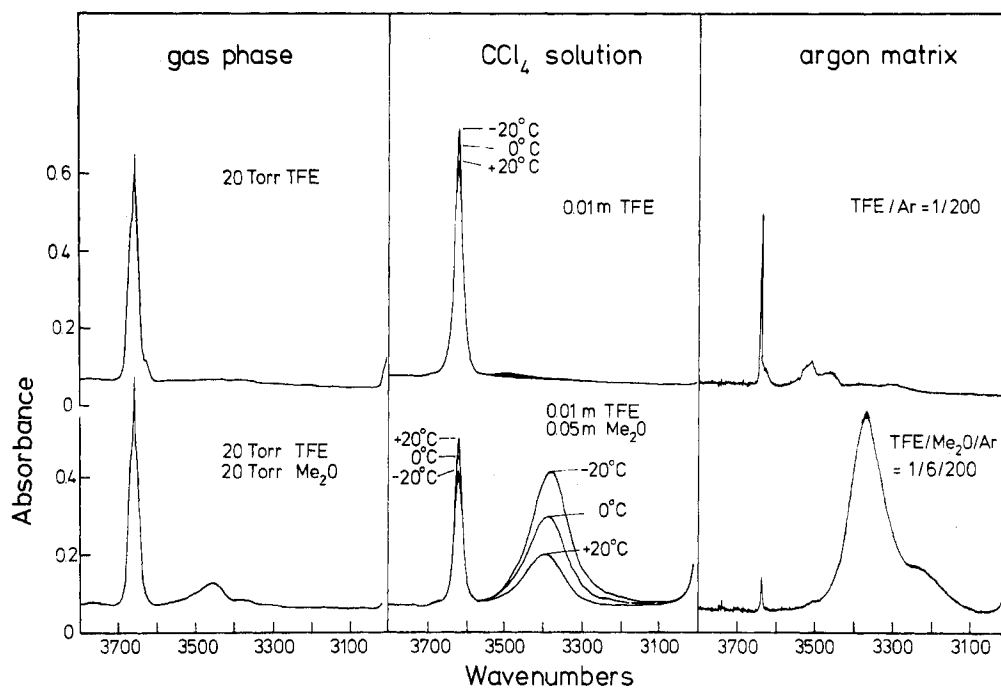
Figure 2. Infrared spectra of 2,2,2-trifluoroethanol (TFE) in the gas phase (20 torr of TFE, $T = 15$ °C, $d = 100$ mm), in CCl_4 solution (0.01 M, $T = -20, 0, +20$ °C, $d = 5$ mm), and in an argon matrix (TFE/Ar = 1/200, $T = 6$ K) in the O–H stretching region (upper part) and spectra of mixtures of TFE (20 torr) with DME (20 torr) in the gas phase ($T = 15$ °C, $d = 100$ mm), TFE (0.01 M) with DME (0.05 M) in CCl_4 ($T = -20, 0, +20$ °C, $d = 5$ mm), and TFE with DME in an argon matrix (TFE/DME/Ar = 1/6/200) at 6 K (lower part).
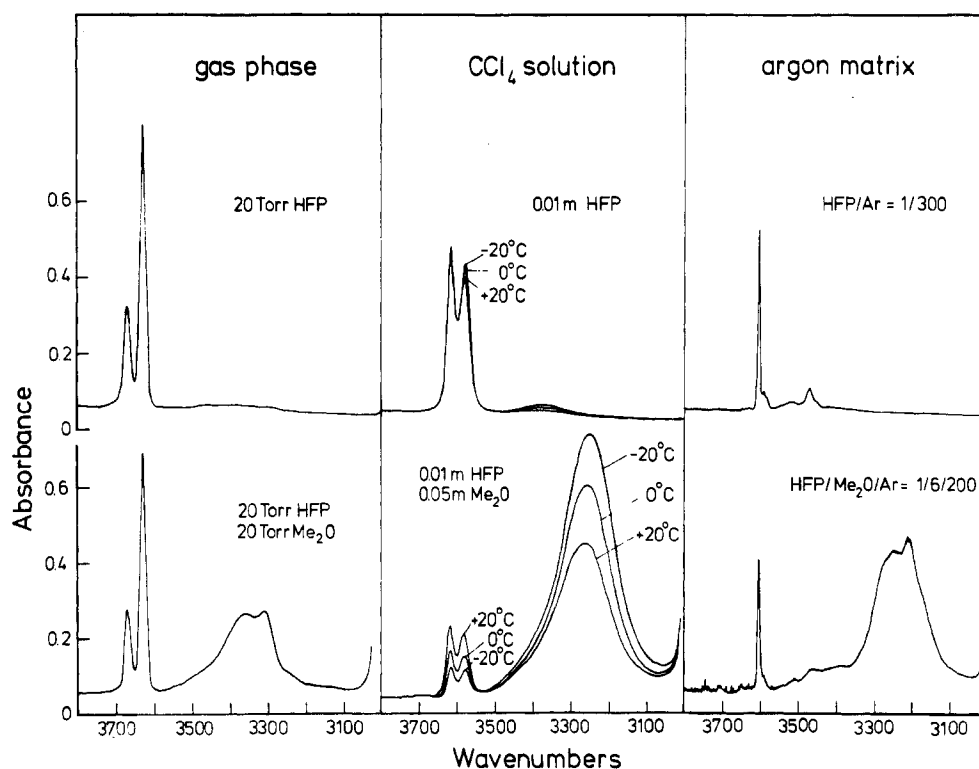
Figure 3. Infrared spectra of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) in the gas phase (20 torr of HFP, $T = 15$ °C, $d = 100$ mm), in CCl_4 solution (0.01 M, $T = -20, 0, +20$ °C, $d = 5$ mm), and in an argon matrix (HFP/Ar = 1/300) at 6 K in the O–H stretching region (upper part) and spectra of mixtures of HFP (20 torr) with DME (20 torr) in the gas phase ($T = 15$ °C), HFP (0.01 M) with DME (0.05 M) in CCl_4 solution ($T = -20, 0, +20$ °C, $d = 5$ mm), and HFP with DME in an argon matrix (HFP/DME/Ar = 1/6/200) at 6 K (lower part).

named possibility should be negligible. On the other hand, it is not always possible to rule out conclusively an interpretation in terms of Fermi resonance. From Figures 1–3 it can be clearly seen that with increasing numbers of fluorine substituents (decreasing pK_a) the frequency shifts $\Delta\nu$ and band intensities as well as the half-widths of the complex bands are increasing. A problem, of course, is the determination of $\Delta\nu$ when either the monomer

or complex band or both are split due to the existence of different conformers. The doublet structure of the complex band of HFP···DME at 3360 and 3310 cm^{-1} (Figure 3), for example, is insensitive to changes of the partial pressures but its intensity ratio is sensitive to temperature variations. Therefore, it can be concluded that both features arise from 1:1 complexes, most likely with HFP in the C_1 and C_s conformational forms as in the free

TABLE I: OH-Stretching Frequencies (cm^{-1}) of the Alcohol Monomers in the Gas Phase, Argon Matrix, and CCl$_4$ Solution[a]

alcohol		ν_g	ν_{Ar}	ν_{CCl_4}	$\nu_g - \nu_{Ar}$	$\nu_g - \nu_{CCl_4}$
CH$_3$CH$_2$OH	EtOH	3677	3660.5	3635 (asym)	16.5	42
			3655.6			
CH$_2$FCH$_2$OH	FE	3660	3645	3618	15	42
			3648	3637 (sh)		
			3642			
			3668			
CHF$_2$CH$_2$OH	DFE	3659	3643	3619	16	43
(CH$_2$F)$_2$CHOH	DFP	3655	3636.5 (s)	3618	18.5	37
		3629	3629 (w)	3598		
			3619 (s)			
			3616.5 (sh)			
CF$_3$CH$_2$OH	TFE	3658	3639.5 (sym)	3618 (sym)	18.5	40
CHF$_2$CF$_2$CH$_2$OH	TFP	3663 (sh)	3641			
		3658.5	3639	3618 (asym)	19.5	40.5
		3629 (w)	3636			
(CF$_3$)$_2$CHOH	HFP	3665		3618		47
		3625	3603.5 (vs)	3579	21.5	46
			3590 (w)			
(CF$_3$)$_3$COH	PFTB	3630	3608	3577	22	53

[a] $\nu_g = \nu_{OH}$ from gas phase, $\nu_{Ar} = \nu_{OH}$ from argon matrix, $\nu_{CCl_4} = \nu_{OH}$ from CCl$_4$ solution (T = 293 K). s = strong, vs = very strong, w = weak, sh = shoulder, sym = symmetric, asym = asymmetric.

TABLE II: OH-Stretching Frequencies (cm^{-1}) of ROH$\cdots$O(CH$_3$)$_2$ Complexes and Frequency Shifts from That of the Free Alcohols in the Gas Phase, CCl$_4$ Solution, and Argon Matrix

alcohol		gas phase		CCl$_4$ solution[a]		Ar matrix[a]	
		ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
CH$_3$CH$_2$OH	EtOH	3567	110	3503	132	3446	209.5
						3452 (sh)	
CH$_2$FCH$_2$OH	FE	3503	157	3460	158	3418	227
CHF$_2$CH$_2$OH	DFE	3479	183	3420	199	3405	238
(CH$_2$F)$_2$CHOH	DFP	3465	185	3411	207	3398	238.5
						3372	244
CF$_3$CH$_2$OH	TFE	3456	202	3395	223	3365	274.5
CF$_2$HCF$_2$CH$_2$OH	TFP	3462	196	3394	224	3382	257
(CF$_3$)$_2$CHOH	HFP	3360	305	3265	353	3254	
		3310	313			3212	391
(CF$_3$)$_3$COH	PFTB	3221	409	3147	461	3120	488

[a] Values for CCl$_4$ solutions are results from measurements at 293 K, for argon matrices at 6 K.

molecules. A similar doublet structure has been found for other HFP$\cdots$base complexes too.[29,30] In the case of the fluorinated ethanols one can proceed on the assumption that the intramolecular hydrogen bond (O–H$\cdots$F) of the gauche form will be broken and in the complexes formed with DME the OH group of the ethanols will be oriented in the trans position. For FE, for example, obviously a small percentage of the free molecule exists in the trans form[22] which could be hidden under the strong R wing of the gauche form at 3660 cm^{-1}. For the estimation of the wavenumber displacements $\Delta\nu$ it would be desirable to refer to the O–H frequencies of the monomeric isomer which corresponds to the conformation of the alcohols in the complexes, i.e., the trans form for the ethanols. However, the frequencies of the monomeric trans form are available only for ethanol and thus we have to refer to O–H frequencies of the gauche form for the fluoroethanols. The monomer frequencies are listed in Table I and the O–H frequencies of the complexes and the wavenumber displacements $\Delta\nu$ are collected in Table II. The temperature dependence of the complex formation shows clearly an increase of the complex band intensities with decreasing temperature as result of a shift of the equilibrium in eq 1 toward the right. Additionally, lowering the temperature also shifts the band maxima a few wavenumbers to lower frequencies, indicating a strengthening of the hydrogen bond.

Solution Measurements

Spectra have been obtained from solutions of the alcohols (0.01 M) in CCl$_4$ and of solutions of the alcohols (0.01 M) with DME (0.05 M) in CCl$_4$. Illustrative examples are shown in Figures 1–3.

Complex formation by fluoroalcohols with ethers in solution is of considerable interest as these alcohols form stable, distillable complexes with alkyl ethers (see ref 21 and 31). The formation of such complexes in solution has been studied to some extent (see ref 14 and references therein). So far, however, DME, which is a gas at room temperature, has not been used as a reference base in solution studies. A relationship between the enthalpy of vaporization of the solute molecules and the intermolecular forces between solute and solvent molecules recently described by Luck[32] allows the approximate prediction of the solubility of DME in CCl$_4$. Our spectroscopic results from the fluoroalcohol monomers and on complex formation with DME in CCl$_4$ are collected in Tables I and II. As can be seen from the spectra in Figures 1–3, the association bands in the ternary mixtures exhibit only a simple contour and one may reasonably assume the value of $\Delta\nu$ primarily to reflect the association in 1:1 complexes. The complex formation is indicated by reduced monomeric O–H absorptions, the appearance of the complex bands, and their strong temperature dependency.

The equilibrium constant for the association of an alcohol with a base B to form a complex of the type R$_3$COH$\cdots$B is defined by

$$K_{11} = [R_3COH\cdots B]/([R_3COH][B]) \qquad (2)$$

where the concentrations are molar concentrations at equilibrium and the activity coefficients have been neglected.[13,33,34] If $C_A{}^0$

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TABLE III: Values of n_F, pK_a, $\sum\sigma^*$ for Ethanol and Fluoroalcohols and $\Delta\nu/\nu$, K_{11}, $\Delta H°$, and $\Delta S°$ Values for ROH···O(CH$_3$)$_2$ 1:1 Complex Formation in CCl$_4$ Solution

alcohol	$n_F{}^a$	pK_a	$\sum\sigma^{*\,b}$	100 $\Delta\nu/\nu$	K_{11}(293 K), L mol^{-1}	$-\Delta H°$, kJ mol^{-1}	$-\Delta G°$, kJ mol^{-1}	$-\Delta S°$, J mol^{-1} K^{-1}
CH$_3$CH$_2$OH	0	15.9	−0.10	3.63	2.81	8.3	2.52	19.67
CH$_2$FCH$_2$OH	1	14.5	+0.24	4.36	1.57	11.8	1.10	36.50
CHF$_2$CH$_2$OH	2	13.3	+0.58	6.16		15.1^c		
CF$_3$CH$_2$OH	3	12.4	+0.92	6.19	5.67	18.2	4.23	47.42
(CF$_3$)$_2$CHOH	6	9.3	+1.84	9.89	30.19	27.4	8.3	66.06
(CF$_3$)$_3$COH	9	5.4	+2.76	12.88	81.23	36.9	10.7	89.5

^{a} Number of Fluorine atoms in the β-position of the alcohols. ^{b} Taft substituent constant. ^{c} Extrapolated from Figure 4.

is the initial concentration of the alcohol, $C_B{}^0$ is that of the base, and A_0 and A are the absorbances at the frequency of the stretching vibration of the monomeric hydroxyl group before and after complex formation, respectively, one can calculate K_{11} from the expression

$$K_{11} = \frac{1 - A_0/A}{A/A_0[C_B{}^0 - C_A{}^0(1 - A/A_0)]} \quad (3)$$

Values for $-\Delta H$ were obtained from plots of log K_{11} vs. $1/T$ according to

$$\ln K_{11} = -\Delta H/RT + \text{constant} \quad (4)$$

by the method of least squares. The quantities $\Delta G°$ and $\Delta S°$ were obtained from the equations

$$\Delta G° = -RT \ln K_{11} \quad (5)$$

$$\Delta S° = (\Delta H° - \Delta G°)/T \quad (6)$$

The values of the thermodynamic quantities, $\Delta\nu/\nu$, Taft substituent parameters, σ^*, and pK_a are collected in Table III.

As can be seen from Figures 1–3, the intensity of monomeric O–H stretching bands is increasing with decreasing temperature in the binary alcohol solutions. It is important for the estimation of K_{11}, according to eq 3, to take this temperature effect and the change in density (absorbances have been density corrected) into account. For ethanol and FE, this effect is stronger than the decrease of the OH band due to complex formation. For all the other alcohols investigated, the drop of the OH band intensity predominates as a consequence of the increasing tendency for complex formation with increasing number of fluorine substituents. It is well-known that CCl$_4$ is not as "inert" as a solvent for hydrogen-bonding studies as would be desired. Kivinen et al.[35] take the view that the usually observed variations of the molar absorption coefficient ϵ of the O–H stretching modes with temperature may, at least partly, arise from O–H···Cl interactions. From Figure 3 it can be seen, for example, that for HFP the free OH absorption also shows a doublet structure in CCl$_4$ as in the gas phase. However, the relative intensities of the two peaks are the reverse of those in the vapor. The enthalpy difference between the two conformers in CCl$_4$ is reported to be 0.6 kJ mol^{-1},[36] whereas it is 4.6 kJ mol^{-1} in the vapor. Thus, OH···Cl interactions seem to stabilize the higher-energy conformer of HFP in CCl$_4$. In the ternary mixtures, the temperature decrease causes a strong intensity increase of the complex bands and simultaneously a decrease of the monomer absorptions, indicating a strong shift of the equilibrium in eq 1 toward the right. Temperature decrease, however, does not only influence O–H band intensities but also shifts monomer and complex absorptions to lower frequencies. Within the temperature range measured (+20 to −20 °C) the monomer O–H bands shift at an average rate of −0.08 cm^{-1} K^{-1} and the complex bands with −0.27 cm^{-1} K^{-1}. This effect has been described as being due to changes in density of the solution.[37,38]
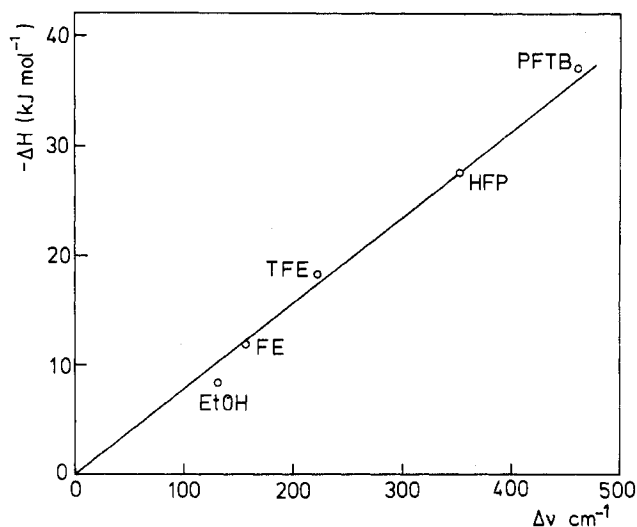

Figure 4. Plot of $-\Delta H$ vs. frequency shift $\Delta\nu$ (Badger–Bauer correlation) for ROH···DME complexes in CCl$_4$ solution [$\Delta\nu = \nu_{OH(free)}(CCl_4) - \nu_{OH(bonded)}(CCl_4)$].

Since all the complex bands in CCl$_4$ are smooth without fine structure the solution spectra do not allow a distinction between conformationally different complex species. However, in cases where the complex bands show asymmetry, it is reasonable to assume that the band consists of superimposed but unresolved absorptions of complexes with different conformational structures. For alcohols which form strong hydrogen bonds with DME, like HFP or PFTB, we have to keep in mind also the possibility of 2:1 complex formation, where two ROH molecules are attached to the ether oxygen. From the position of the absorption maximum we get, therefore, only an average value for $\Delta\nu$. From the observations described above it is obvious that it is necessary to be familiar with solvent effects as well as temperature effects in solution studies for a given system before correlations are used. Concerning solvent shift theories and experimental studies on solvent effects, we refer to reviews on this subject.[39–42]

Values of $-\Delta H$ for the complexes studied are plotted according to the Badger–Bauer relation[43,44] against $\Delta\nu$ ($\Delta\nu = \nu_{OH(free)}(CCl_4) - \nu_{OH(bonded)}(CCl_4)$) in Figure 4. A good linearity is evident and the line passes through the origin. The following correlation was found:

$$-\Delta H(\pm 2) \text{ (kJ mol}^{-1}) = 0.0776\Delta\nu \text{ (cm}^{-1}) \quad (7)$$

From plotting $-\Delta H$ against $-\Delta S$ a moderately linear correlation was obtained. This is common for hydrogen-bonded systems; thus, Pimentel and McClellan[45] have discussed the significance of the

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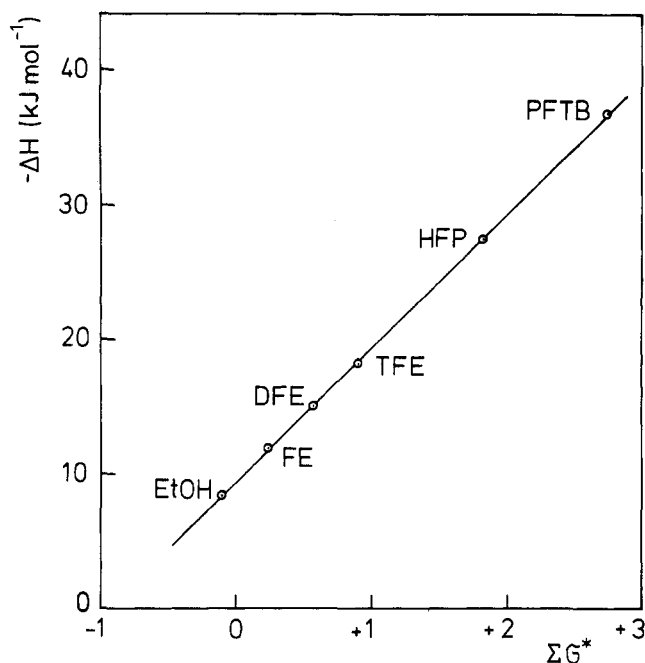
Figure 5. Plot of $-\Delta H$ vs. the sum of Taft's substituent constants $\sum\sigma^*$ with $-\Delta H$ determined from the measurements in CCl_4 solution.

$-\Delta H$ vs. $-\Delta S$ relation and refer to cases in which the linearity of the enthalpy–entropy relation holds. The explanation given by Pimentel and McClellan[45] for hydrogen-bonded systems, that "a higher value of $-\Delta H$ implies stronger bonding, with a more restricted configuration, hence greater order leading to a larger value of $-\Delta S$", is widely cited. For the complexes reported here, it may be suggested that the stiffness of the complex, which increases with increasing hydrogen bond strength, may contribute to the entropy term. The influence of the acidity of the alcohols on the hydrogen bond strength and therefore spectroscopic quantities is very distinct, as it can be seen from Figures 1–3 and Tables I–III. The pK_a values of ordinary alcohols vary only very little. However, drastic changes are observed with increasing number of fluorine substituents as indicated by the decrease of the pK_a values listed in Table III. It is clear from our results that the more acidic an alcohol is the more marked is the tendency to form hydrogen bonds with acceptors. This leads to increasing values of the spectrometric parameters K_{11}, $-\Delta H$, and $\Delta\nu_{OH}$.[46–48] We have obtained linear dependencies by plotting $\Delta\nu$ and $-\Delta H$ against the pK_a values of the alcohols. As it has been shown by Sherry et al.[18] a plot of pK_a vs. σ^* of various fluorinated alcohols gives a good fit. Thus, we can correlate the sum of Taft's σ^* substituent constants with $-\Delta H$. As it can be seen from Figure 5 the linearity is excellent and from the plot we can derive the following relation

$$-\Delta H(\pm 1)\ (kJ\ mol^{-1}) = 9.75\sum\sigma^* + 9.35 \qquad (8)$$

which allows predictions of $-\Delta H$ for further $ROH\cdots O(CH_3)_2$ complexes in a simple manner, since there is access to σ^* values in the literature. We do not intend to discuss other possible frequency shift correlations obtainable from our data and refer to the survey by Joesten and Schaad.[42]

Measurements in Argon Matrices

Again, as a first step the spectra of ethanol and the fluoroalcohols isolated in solid argon have been recorded at 6 K. Infrared matrix spectra have been reported in the literature already for

$EtOH,^{49,50}$ $FE,^{51}$ $DFE,^{52}$ $TFE,^{7,53}$ $DFP,^1$ $HFP,^{26}$ and $PFTB.^{28}$ As can be seen from Figures 1–3 the O–H stretches of the monomers look quite different in argon matrices compared to those in the gas phase and solution spectra. The bands are much narrower in the matrices than in the two other phases. Under the experimental conditions used ($ROH/Ar = 1/200$) small amounts of dimers are also present which absorb in the 3500-cm^{-1} range.

Spectral changes which are produced in solid solution generally resemble those that accompany the dissolution of molecules in liquid solvents, but there are several additional effects which arise from the matrix environment. Like in solutions the isolated molecules of complexes are subject to solute–matrix interactions. These will perturb the solute's vibrational energy levels and be reflected in a frequency shift

$$\Delta\nu = \nu_{gas} - \nu_{matrix}$$

which is analogous to a solvent shift and, for stretching modes, is usually to lower frequencies. Like the solvent shift, the matrix-induced shift is an overall sum of bulk dielectric effects, dispersions, and specific solute–matrix interactions.[54] Matrix shifts can thus provide an important source of information concerning the molecular interactions between absorber molecules and surrounding molecules. We have discussed the problem of host–guest interactions in rare gas and molecular matrices in some detail in a separate paper.[55]

For some of the monomeric alcohols isolated in matrices we have clear evidence for the existence of different conformers, like in the case of FE (3648, 3645, 3642 cm^{-1}: O–H absorptions due to the Gg' conformer; 3668 cm^{-1}: absorption of the Tt conformer), where there is hardly any indication for more than one conformer in the gas phase or CCl_4 solution. FE isolated in matrices is an interesting system, since it shows conformational interconversion in matrices when exposed to infrared irradiation.[51,56–58] EtOH exists also in the trans and gauche form (3655.5, 3660.5 cm^{-1}) and DFP in the C_1 and C_s form (3636.5, 3619 cm^{-1}). On the other hand, however, monomeric HFP shows only one O–H stretching mode in argon matrix (3603 cm^{-1}) while in the gas phase and in CCl_4 solution it shows a doublet due to the coexistence of C_1 and C_s conformers. Apparently, only the C_s conformer exists in the argon matrix. For DFE, TFE, TFP, and PFTB only one conformational form is observed for the monomeric species in argon matrices.

For the study of the complexes in argon matrices we used an excess of ether ($ROH/DME/Ar = 1/6/200$) to avoid self-association of the alcohols in the matrix and to increase the probability for the formation of $ROH\cdots DME$ 1:1 complexes. As recently discussed by Andrews[59] the low-temperature matrix helps stabilizing the complexes by holding the donor and acceptor molecules together in a rigid cage, while internal energy is removed on condensation of the matrix. As can be seen from Figures 1–3 very intense complex bands appear in the mixtures, whereas the monomer absorptions are diminishing. Some of the complex bands are fairly symmetric, e.g., for the TFP···DME complex, while others show a second component on the low-frequency side of the complex band. These shoulders have most likely to be assigned to contributions from 2:1 complexes of the type $ROH\cdots ROH\cdots DME$. In some cases, like for FE, DFP, TFP, and HFP, the

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complex bands show fine structure due to conformational multiplicity of the complexes. These different conformational structures of the complexes resemble the possible conformational structures of the alcohols in their monomeric forms as described above. We also observe intensity changes in the fine structure of the complex bands on annealing the matrices, accompanied by a growth of the energetically favored conformational structure (thermally induced interconversions). Additionally, sharpening of the complex bands and a shift to lower frequencies occurs as a consequence of annealing. As previously stated,[20] we believe that this effect arises from a more favorable orientation of the complexes and/or closer packing in the matrix after the annealing process. As it can be seen for the HFP···DME complex in Figure 3, there is a close resemblance in some cases between the complex band profiles of the gas-phase and matrix spectra. The O–H frequencies of the complexes are summarized in Table II and the monomer frequencies in Table I. In a first approximation, the gas to matrix shifts ($\Delta\nu_{matrix} - \Delta\nu_{gas}$) observed for the complexes are constant and are found to be on the order of 66 ± 13 cm^{-1}. From Table I it can be seen that monomeric O–H stretches, on the other hand, are shifted only 19 ± 4 cm^{-1} as one passes from the gas phase to argon matrices. By comparing the three phases it becomes quite obvious that the hydrogen bond interactions are strongest in the argon matrices since the $\Delta\nu$ values are considerably higher than those in CCl$_4$ solution, presumably as the result of reduced O···O bond distances in the low-temperature solid.

Conclusions

Infrared spectra of molecular complexes of fluoroalcohols with simple reference bases like DME in different phases provide information primarily from the O–H stretching frequencies relating to the hydrogen bond donor ability of the alcohols, hydrogen bond strengths, conformational structures of the complexes, and environmental effects. Concerning the monomer absorption we were able to show that the shift induced by the argon matrix (19 ± 4 cm^{-1}) is approximately only half of the shift caused by the CCl$_4$ environment (45 ± 8 cm^{-1}). As anticipated, the ratio of these shifts reflects, within the limits of error, the ratios of the square roots of the critical temperatures (T_c) of argon and CCl$_4$

$$T_{c(Ar)}^{1/2} / T_{c(CCl_4)}^{1/2} = 0.52$$

Concerning the fluoroalcohol···DME complexes one can say that they are an ideal model system for the study of proton donor–acceptor interactions, since only inductive effects have to be considered and mesomeric effects can be ruled out. Depending on the degree of fluorination, the acidity can be varied over a wide range. Each introduction of a fluorine substituent in the β-position of the alcohols increases the acidity systematically, causing a stepwise increase of $\Delta\nu$ in the complexes (see Figure 6). In the gas phase, where no additional intermolecular interactions need to be considered, this increase is 34 ± 13 cm^{-1} for each fluorine added to the alkyl part of the alcohol. Studies in solutions, where quantitative measurements can be made very precisely, on the other hand, have the advantage of providing the most reliable thermodynamic data, whereas matrices enable small frequency shifts or splittings to be observed, from which in many cases the
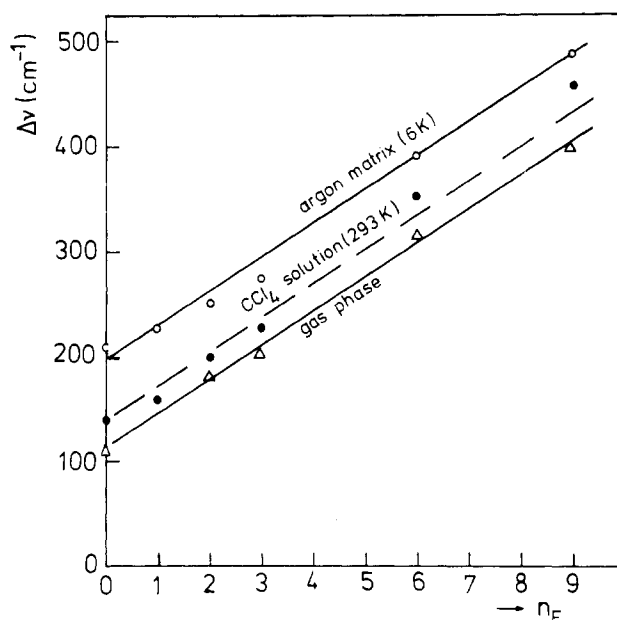

Figure 6. Plot of frequency shifts $\Delta\nu$ obtained from the gas phase, CCl$_4$ solution, and argon matrix vs. the number of fluorine atoms (n_F) in the β-position of the alcohols: (O) values from argon matrices at 6 K; (●) values from CCl$_4$ solutions at 293 K; (△) values from the gas phase.

conformational structure of the complex may be deduced. Therefore, the combined results from the various phases (gas, liquid solution, solid solution) give a deeper insight into the details of intermolecular attracting forces ranging from very weak to very strong and provide more detailed structural information. It is shown that the strength of the O–H···O bonds in the ROH···O-(CH$_3$)$_2$ complexes increases stepwise with increasing values of the sum of Taft's substituent constants $\sum\sigma^*$. $\sum\sigma^*$ values are therefore a measure for the proton donor strength as is the frequency shift $\Delta\nu_{OH}$. Increasing donor strength is accompanied by a decrease in the acceptor strength of the alcohol oxygens, as indicated by decreasing values for the proton affinities. This fact usually leads to a reduced tendency for self-association. With the knowledge of $\sum\sigma^*$, frequency shifts and hydrogen bond strengths can now be predicted quantitatively for related systems, based on the results reported here. It is suggested that studies of fluoroalcohol···base complexes in matrices with stronger proton acceptors may lead to situations where proton sharing or even proton transfer can be observed.